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Asymptotic Approximations to the Distributed Activation Energy Model

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Abstract—We present approximations to the Distributed Activation Energy Model (DAEM), also known as the Multiple Reaction Model (MRM), which is widely used in complex chemical systems such as coal pyrolysis. MRM assumes that the process can be represented by a continuum distribution in activation energy of individual reactions. An individual reaction is characterised by a pre-exponent coefficient and an activation energy. The distribution, usually Gaussian, is over the activation energy. The solution for the amount of product requires the evaluation of a double integral. This paper develops asymptotic approximations to this double integral, based on the assumptions that the mean of the Gaussian is large and that its standard deviation is small. The method will have wide applicability in situations, such as computational fluid dynamics modelling of coal-fired boilers, where it is important to be able to evaluate this double integral quickly. It also provides analytical insights into solution behaviour, since the asymptotic forms are explicit.

Keywords—Multiple reaction model, Distributed activation energy, Devolatilisation, Asymptotic expansion, Coal pyrolysis.

1. INTRODUCTION

The Distributed Activation Energy Model (DAEM) or Multiple Reaction Model (MRM) for coal pyrolysis [1] may be applied to either the total amount of volatiles released, or to the amount of an individual volatile constituent like carbon monoxide or tar. It is also called the Distributed Rate Model, and adapts Vand's treatment of independent parallel processes [2] in modelling the resistance of metallic films. We will refer to the model as the MRM in this paper. The description here follows the development for the total amount of volatiles in [1] and [3]. The thermal decomposition due to a particular reaction i within the coal structure is modelled as a first-order irreversible reaction, with the mass of reacted or released volatile V_i taken to vary in

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time t according to the equation

$$\frac{dV_i}{dt} = k_i(V_i^* - V_i), \tag{1}$$

where V_i^* is the total mass of volatile originally available for reaction, so that $V_i^* - V_i$ is the amount of unreacted volatile remaining at time t. The reaction rate k_i is taken to be of Arrhenius form,

$$k_i(t) = k_{0i}e^{-E_i/(RT(t))}, \tag{2}$$

where $T(t)$ is the time varying absolute temperature of the coal, $R = 8.3$ J/K is the universal gas constant, E_i is the activation energy, and k_{0i} is the pre-exponential factor. Values of k_{0i}, E_i, and V_i^* are estimated from matching to experimental data. While the theoretical work developed here allows for a rather general temperature variation with time, typical experiments use a constant ramping rate $\frac{dT}{dt}$.

The solution to equation (1) may be written in terms of the mass of volatiles remaining to be released at time t,

$$\frac{V_i^* - V_i}{V_i^*} = \exp\left(-\int_0^t k_i(u)\,du\right). \tag{3}$$

Early modelling was based on just one reaction ($i = 1$). Some materials can be accurately modelled by a single reaction scheme, with k_0 and E_0 fitted to a series of experiments conducted at different heating rates. However, more complicated reactions like coal pyrolysis cannot be adequately modelled by a single reaction, due to large variations in the values of k_0 and E_0 with the heating rate $\frac{dT}{dt}$ [4–6].

One approach is to consider many single reactions, and to assume that the k_is differ only in activation energy, that is, that $k_{0i} = k_0$ for all i, and that E_i may be represented as a distribution $F(E)$. The fraction of potential total volatile loss that has an activation energy between E and $E + dE$ is represented by $F(E)\,dE$. Then, V_i^* and V_i are replaced by $dV^* = V^*F(E)\,dE$ and $dV = VF(E)\,dE$, respectively, in equation (3), and the equation is integrated over E to get

$$\frac{V^* - V}{V^*} = \int_0^\infty \exp\left[-k_0\int_0^t e^{-E/RT}\,dt\right] F(E)\,dE. \tag{4}$$

A popular choice for F is the Gaussian distribution with mean E_0 and variance σ,

$$F(E) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left(\frac{-(E - E_0)^2}{2\sigma^2}\right). \tag{5}$$

Hence, the solution for the MRM model is

$$v \equiv \frac{V^* - V}{V^*} = \frac{1}{\sigma\sqrt{2\pi}}\int_0^\infty \exp\left[-k_0\int_0^t e^{-E/RT}\,dt - \frac{(E - E_0)^2}{2\sigma^2}\right] dE. \tag{6}$$

2. ASYMPTOTIC EXPANSIONS

We seek approximations to v which avoid the double integration, as there are some applications which require many evaluations of v. One approximation is a narrow Gaussian or $\sigma \to 0$. Another is that E_0/RT is large.

2.1. Energy or Small σ Expansions

When $\sigma \to 0$, Laplace's method can be used [7] to expand the outer integral, which is in the Laplace form

$$v(x) = \int_0^\infty f(E)\exp(xg(E))\,dE\, x \to \infty, \tag{7}$$

where

$$f(E) \equiv \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-k_0 \int_0^t \exp\left(\frac{-E}{RT(t')}\right) dt'\right), \tag{8}$$

and

$$g(E) \equiv -\frac{(E-E_0)^2}{2}, \tag{9}$$

and $x \equiv 1/\sigma^2$.

The function $g(E)$ takes its maximum at E_0, so we expand f in a Taylor series about E_0,

$$\begin{aligned} f(E) \sim \frac{1}{\sigma\sqrt{2\pi}} \Big[& f(E_0) + (E-E_0)f'(E_0) + (E-E_0)^2 f''\frac{(E_0)}{2} \\ & + (E-E_0)^3 f'''\frac{(E_0)}{6} + (E-E_0)^4 f^{iv}\frac{(E_0)}{24}\Big], \qquad E \to E_0. \end{aligned} \tag{10}$$

Here we define

$$e_j(E) \equiv \int_0^t e^{-E/RT(t')} \frac{dt'}{(RT(t'))^j}, \qquad j = 0, 1, 2 \ldots, \tag{11}$$

and noting that

$$\frac{de_j}{dE} = -e_{j+1}, \tag{12}$$

we have

$$f(E_0) = \exp(-k_0 e_0), \tag{13}$$

$$f'(E) = k_0 e_1 e^{-k_0 e_0}, \tag{14}$$

$$f''(E) = e^{-k_0 e_0}\left[(k_0 e_1)^2 - k_0 e_2\right], \tag{15}$$

$$f'''(E) = e^{-k_0 e_0}\left[(k_0 e_1)^3 - 3k_0^2 e_1 e_2 + k_0 e_3\right], \tag{16}$$

and

$$f^{iv}(E) = e^{-k_0 e_0}\left[(k_0 e_1)^4 - 6k_0^3 e_1^2 e_2 + 3k_0^2 e_2^2 + 4k_0^2 e_1 e_3 - k_0 e_4\right]. \tag{17}$$

Laplace's method involves approximating v by reducing the range of integration to the neighbourhood of E_0, expanding about E_0, and sending the range of integration to $\pm\infty$ for evaluation, so that the leading term is

$$v(\sigma) \sim v_0(\sigma), \tag{18}$$

where

$$v_0(\sigma) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-k_0 \int_0^t \exp\left(\frac{-E_0}{RT(t')}\right) dt'\right) \int_{-\infty}^{\infty} \exp\left(\frac{-(E-E_0)^2}{2\sigma^2}\right) dE, \qquad \sigma \to 0. \tag{19}$$

The energy integral evaluates to $\sigma\sqrt{2\pi}$, so that the leading behaviour is

$$v_0 = \exp\left[-k_0 \int_0^t e^{-E_0/(RT(t'))}\, dt'\right], \qquad \sigma \to 0. \tag{20}$$

This is the same as the solution that is obtained for the simplest first-order model with a single activation energy E_0, by just taking $i = 1$ above. It may alternatively be obtained by replacing the distribution $F(E)$ by a delta function $F = \delta(E - E_0)$.

Odd terms f', f''' do not contribute to the asymptotic behaviour of v, since the integrands are odd functions, giving integrals that evaluate to zero.

Then $v - v_0 \sim v_2\ \sigma \to 0$, where

$$v_2 = \frac{v_0 k_0 f''(E_0)}{2\sigma\sqrt{2\pi}} \int_{-\infty}^{\infty} (E - E_0)^2 \exp\left(\frac{-(E-E_0)^2}{2\sigma^2}\right) dE. \tag{21}$$

The integral evaluates to $\sqrt{2\pi}\,\sigma^3$, so that

$$v_2 = v_0 k_0 f''(E_0)\frac{\sigma^2}{2}. \tag{22}$$

To second order then, we have

$$\begin{aligned} v \sim \exp&\left[-k_0 \int_0^t e^{-E_0/(RT(t'))}\, dt'\right] \\ &\left[1 + \frac{k_0\sigma^2}{2}\left(k_0\left\{\int_0^t e^{-E_0/RT}\frac{dt'}{RT}\right\}^2 - \int_0^t e^{-E_0/RT}\frac{dt'}{R^2T^2}\right)\right], \qquad \sigma \to 0. \end{aligned} \tag{23}$$

The next term is fourth order in $E - E_0$, and is calculated in a similar manner, giving the term $(\sigma^4/8)f^{iv}(E_0)$, and we have

$$v \sim f(E_0) + \frac{\sigma^2}{2}f''(E_0) + \frac{\sigma^4}{8}f^{iv}(E_0), \qquad \sigma \to 0. \tag{24}$$

2.2. Time or Large Energy Expansions

We seek asymptotic expansions for the time integrals that remain, assuming that the mean activation energy is large, in particular, that $E_0/(RT_0) \to \infty$, where T_0 is a representative temperature. This will help to see what size the derivative terms in f are, and it will also speed up the evaluation of v.

Temperature $T(t)$ (and hence, the function $-1/T$, which has the same shape) is typically monotonic increasing until the reaction is finished. We rescale $T(t) = T_0\tau(t)$, and take $z = E_0/(RT_0) \to \infty$.

Then,

$$\int_0^t e^{-E_0/(RT(t'))}\, dt' = \int_0^t e^{-z/\tau(t')}\, dt', \tag{25}$$

and the exponent function $-1/\tau$ has its maximum value at t. Noting the expansion (as $t' \to t$)

$$\frac{-1}{\tau(t')} \sim \frac{-1}{\tau(t)} + (t'-t)\frac{\tau'(t)}{\tau^2(t)} + \frac{(t'-t)^2}{2}\left(\frac{\tau''(t)}{\tau^2(t)} - 2\frac{(\tau'(t))^2}{\tau^3(t)}\right), \tag{26}$$

equation (25) becomes (as $z \to \infty$)

$$\int_0^t e^{-z/\tau(t')}\, dt' \sim \int_{t-\epsilon}^t e^{-z/\tau(t')}\, dt' \tag{27}$$

$$\sim \int_{t-\epsilon}^t e^{-z/\tau(t)} e^{z(t'-t)\tau/\tau^2} e^{z(t'-t)^2/2\left(\tau''(t)/\tau^2(t) - 2(\tau'(t))^2/\tau^3(t)\right)}, \tag{28}$$

which becomes

$$\sim e^{-z/\tau}\int_{-\infty}^t \exp\left(z(t'-t)\frac{\tau'}{\tau^2}\right)\left[1 + \frac{z(t'-t)^2}{2}\left(\frac{\tau''}{\tau^2} - 2\frac{(\tau')^2}{\tau^3}\right)\right] dt', \tag{29}$$

where all τ functions and their derivatives are evaluated at t.

These integrals may now be evaluated, and the temperature rescaling reversed, to give (as $E_0/(RT_0) \to \infty$)

$$\int_0^t e^{-E_0/(RT(t'))}\,dt' \sim \frac{\exp(-E_0/(RT))}{E_0/(RT)}\left(\frac{T}{T'}\right)\left[1+\left(\frac{RT}{E_0}\right)\left(\frac{T''T}{(T')^2}-2\right)\right], \tag{30}$$

where all T functions and derivatives are evaluated at time t.

The leading term in the above expansion is well known in the literature for single reactions when heating rate is constant (e.g., [5]). The derivation here applies to more general temperature histories, and also indicates the accuracy of the approximation through the second term.

Some care is needed to obtain the second term in the expansions for the remaining integrals in equation (23), as both the exponent and the coefficient functions contribute to second order in $E_0/(RT_0)$. We find that

$$\begin{aligned}\int_0^t e^{-z/\tau(t')}\frac{dt'}{RT(t')} \sim e^{-z/\tau}\int_{-\infty}^t e^{z(t'-t)\tau'/\tau^2}\left(1+\frac{z(t'-t)^2}{2}\left(\frac{\tau''}{\tau^2}-\frac{2(\tau')^2}{\tau^3}\right)+\cdots\right)\\ \cdot\left(\frac{1}{RT}-\frac{(t'-t)}{R}\left(\frac{T'}{T^2}\right)+\cdots\right)dt', \qquad z\to\infty,\end{aligned} \tag{31}$$

where all T and τ terms are to be evaluated at t. The cross terms involving $z(t'-t)^2$ and $t'-t$ both contribute to the second-order asymptotic behaviour. Evaluating the integrals gives

$$\int_0^t e^{-z/\tau(t')}\frac{dt'}{RT(t')} \sim \frac{\exp(-E_0/(RT))}{E_0}\left(\frac{T}{T'}\right)\left[1+\frac{RT}{E_0}\left(\frac{TT''}{(T')^2}-1\right)\right], \qquad z\to\infty \tag{32}$$

and similarly (with both cross terms again contributing at second order),

$$\int_0^t e^{-z/\tau(t'))}\frac{dt'}{R^2T^2(t')} \sim \frac{\exp(-E_0/(RT))}{E_0RT'}\left(1+\frac{RT}{E_0}\left(\frac{TT''}{(T')^2}-1\right)\right), \qquad z\to\infty. \tag{33}$$

To leading order only,

$$\int_0^t e^{-z/\tau(t'))}\frac{dt'}{(RT(t'))^j} \sim \frac{\exp(-E_0/(RT))}{E_0/(RT)}\frac{T}{T'}\frac{1}{(RT)^j}, \qquad j\geq 0, \quad z\to\infty. \tag{34}$$

In summary, the behaviour of v is

$$v \sim v_0+v_1+v_2+v_4, \qquad \frac{E_0}{(RT)} \to \infty, \sigma\to 0, \tag{35}$$

where

$$v_0 = \exp\left[-k_0e^{-E_0/RT}\left(\frac{RT}{E_0}\right)\left(\frac{T}{T'}\right)\right], \tag{36}$$

$$v_1 = -v_0k_0e^{-E_0/RT}\left(\frac{RT}{E_0}\right)^2\left(\frac{T}{T'}\right)^2\left(\frac{T''}{T'}-\frac{2T'}{T}\right), \tag{37}$$

and

$$v_2 = \frac{v_0k_0}{2}e^{-E_0/RT}\left(\frac{RT}{E_0}\right)\left(\frac{T}{T'}\right)\left(\frac{\sigma}{RT}\right)^2\left[k_0e^{-E_0/RT}\left(\frac{RT}{E_0}\right)\left(\frac{T}{T'}\right)-1\right], \tag{38}$$

and

$$v_4 = \frac{v_0\sigma^4}{8}\left[(k_0a_1)^4-6k_0^3a_1^2a_2+3k_0^2a_2^2+4k_0^2a_1a_3-k_0a_4\right], \tag{39}$$

or

$$v_4 = \frac{1}{8}\left(\frac{\sigma}{RT}\right)^4\left[(k_0a_0)^4-6(k_0a_0)^3+7(k_0a_0)^2-k_0a_0\right], \tag{40}$$

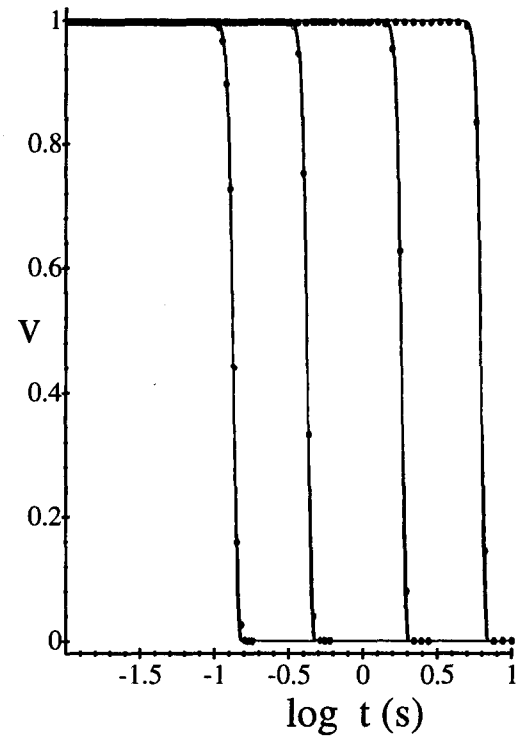

Figure 1. Data and fits for Savage Mine lignite. Circles are the MRM model, solid lines are v_0 and $v_0 + v_2$ (closest to the data). The four different cases correspond to four different heating rates, 10,000, 3000, 650, and 180°C/s from left to right, respectively.

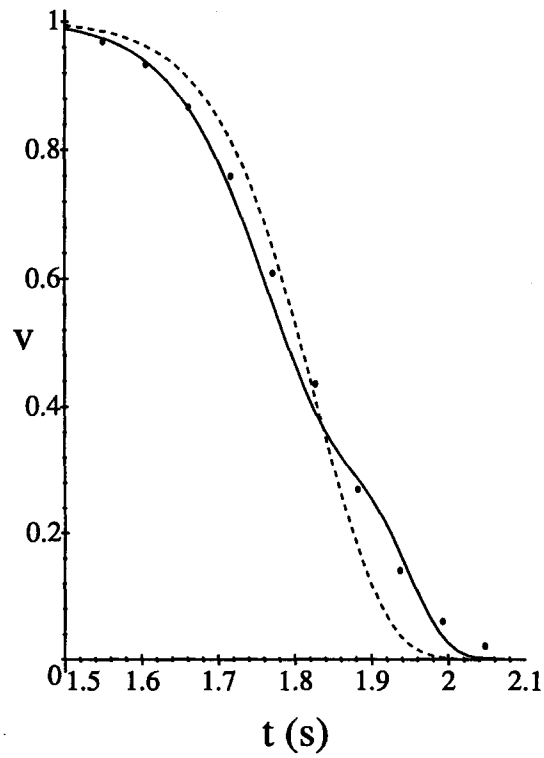

Figure 2. Data and fits for Savage Mine lignite, when heating rate is 650°C/s. Circles are the MRM model, the dashed line is v_0 and the solid line is $v_0 + v_2$

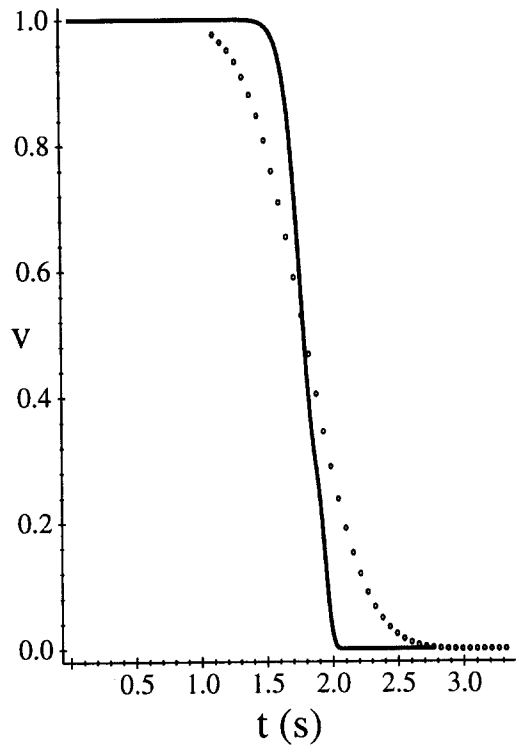

Figure 3. Data and fits for Savage Mine lignite, when heating rate is 650 K/s. Circles are the MRM model using the actual value $\sigma = 40,000$ J fitted to data, solid lines are v_0 and $v_0 + v_2$ (closest to the data) with $\sigma = 10,000$ J.

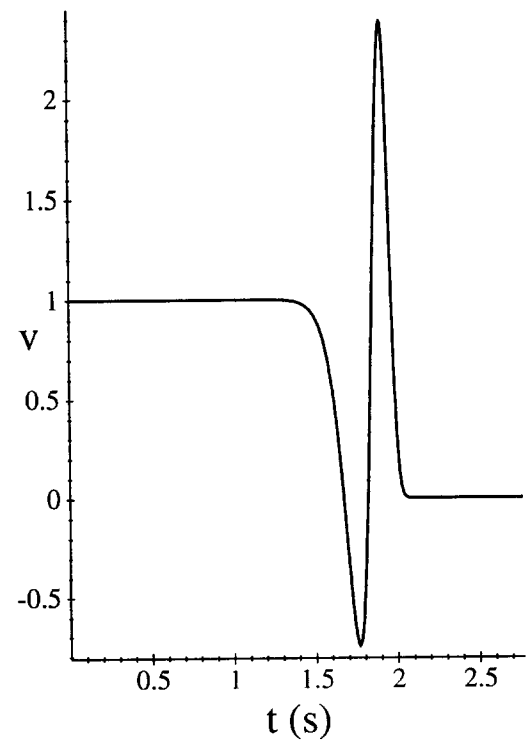

Figure 4. A graph of $v_0 + v_2$ for Savage Mine lignite when $\sigma = 40,000$ J is used, violating the asymptotics.

where

$$a_j \equiv \frac{a_0}{(RT)^j}, \qquad a_0 \equiv \frac{\exp(-E_0/RT)}{E_0/RT}\frac{T}{T'}. \tag{41}$$

ASYMPTOTIC VALIDITY

Comparisons have been made between the values of v computed by doing the double integrals, and the values obtained by using the above asymptotic approximations. Good fits, independent of heating rate, are obtained. Note that while the theory developed applies to any increasing temperature history, the experiments referred to here all have constant heating rates.

For example, in Figure 1, data and fits are presented for pyrolysis of lignite from Savage Mine, Montana [1]. Parameter values used for both data and fits for the Savage Mine lignite are $k_0 = 1.07E10\,\mathrm{s}^{-1}$, $E_0 = 2.05E05\,\mathrm{J/mole}$, and $\sigma = 1.0E04\,\mathrm{J/mole}$. With the exception of σ, which has been reduced from the fitted value of $1.0E04\,\mathrm{J/mole}$ so that $v_2 < v_0$, these are the values fitted to Savage Mine lignite when using the MRM model, as in [1]. Note that reducing σ while holding the other parameters constant has the effect of narrowing the distribution $F(E)$.

The plot shows $v(t)$ against $\log_{10} t$ for various heating rates, calculated using the MRM model integrals (*data* shown as circles), and calculated using v_0 and $v_0 + v_2$ (solid lines). The fits are so close that an expanded view of the 650 K/s case is shown in Figure 2.

In Figure 3, the data (MRM model results) from Savage Mine lignite is presented using the actual fitted value for $\sigma = 40\,\mathrm{kJ/mole}$ from [1]. However, the fits presented use $\sigma = 10\,\mathrm{kJ/mole}$, to illustrate that the asymptotics cannot match the data spread. Heating rate is 650 K/s. In Figure 4, the result of using the (too large) quoted value of σ in the asymptotic expansion $v_0 + v_2$, when heating rate is 650 K/s is shown.

We find that adding the term v_1 makes no observable difference to v_0, indicating that the large activation energy expansion is very accurate at leading order.

4. CONCLUSIONS

Asymptotic analysis has given simpler expressions for the time dependence of volatile release from coal. These simpler expressions apply for arbitrary but monotonically increasing temperatures with time, and are robust under changes of heating rate. They will be much faster to compute, important in models that require many evaluations of v. However, there is a limitation on how large the variance of activation energy may be, due to the approximation that $\sigma \to 0$.

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